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Crystal and Molecular Structure of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$: An Example of Four Alkynic Groups Bonded to a Metal Cluster

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$Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$, obtained from either $Ru_3(CO)_{12}$ or $HRu_3(CO)_9[C_2C(CH_3)_3]$ and 3,3-dimethyl-1-butyne, crystallyzes in the triclinic space group $P\bar{1}$, with a = *11.942(7),* b = *12.877(8),* c = *11.219(7)* Å, *α = 97.86(2), β = 102.41(3), γ = 90.44(1)°, Z = 2; Patterson and Fourier-difference maps revealed the atom positions, all hydrogens included. The refinement, anisotropic only for the ruthenium atoms, led to the final* R = *0.037 for 3687 observed reflections.*

The X-ray structural analysis showed the presence of two organic ligands face-bonded to the triruthenium isosceles cluster. The first ligand originates from two alkynic molecules, each other bonded via a –C–O– bridge, to form with an Ru–Ru bond two penta-atomic adjacent rings. The second consists of a chain formed by two head-to-tail joined alkynic moieties.

Introduction

Two isomeric forms of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ were obtained as minor products during the reaction of $Ru_3(CO)_{12}$ or $HRu_3(CO)_9[C_2C(CH_3)_3]$ with 3,3-dimethyl-1-butyne [1, 2]; the unusually high number of alkynic moieties in these molecules prompted us to undertake an X-ray study of one of them with the aim to shed more light on the various types of bonding of unsaturated ligands with the metallic frame.

The present diffraction study, together with the X-ray [3], neutron [4] and ^{13}C n.m.r. [5] analyses of $HRu_3(CO)_9[C_2C(CH_3)_3]$, is part of a structural research on mono- and poly-acetylenic derivatives of osmium and ruthenium carbonyls [6–9].

Experimental

X-Ray Data Collection

Deep-green crystals of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ were obtained by crystallization from a n-heptane solution at −10 °C, and a crystal sealed in a glass capillary under nitrogen atmosphere was used for the collection of all the data. Preliminary Weissenberg photographs showed triclinic symmetry; the centrosymmetric space group $P\bar{1}$ was assumed initially and confirmed by the successful solution and refinement of the structure. The cell parameters were determined from least-squares refinement of the θ angles of 15 reflexions accurately centered on a Philips PW 1100 four-circle automatic diffractometer. The crystal data are: $a = 11.942(7)$, $b = 12.877(8)$, $c = 11.219(7)$ Å, $\alpha = 97.86(2)$, $\beta = 102.41(3)$, $\gamma = 90.44(1)°$, $V = 1667.87$ Å^3, $M = 827.86$, $Z = 2$, $D_c = 1.65$ g cm^{-3}, $D_m = 1.66$ g cm^{-3}, $\mu = 13.69$ cm^{-1}.

A total of 4351 unique reflexions were collected up to 2θ equal 45° on the same Philips diffractometer using the ω-scan technique (MoKα radiation, graphite monochromatized, λ = 0.71069 Å), scan speed 0.07° sec^{-1}, each scan-width 1.00°, background measured for 3 sec on both sides of each peak. Intensities of three standard reflections (223), $(\overline{2}\overline{4}3)$, (124) were measured after every 450 reflexions and showed no significant variation during data collection.

Solution and Refinement of the Structure

The positions of the three ruthenium atoms, located from a three-dimensional Patterson synthesis using the 4351 collected intensities, were refined by least-squares cycle [10] to the discrepancy factor:

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.253.$$

Atomic scattering factors were those of Cromer and Waber [11]. Subsequent Fourier-difference maps revealed all the remaining non-hydrogen atoms; the isotropic refinement of all these atoms gave $R = 0.084$.

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TABLE 1. Fractional Positional Coordinates and Thermal Parameters (Å^2) for $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$, with the Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c	B
Ru(1)	0.05495(4)	0.25482(4)	0.23586(5)	*
Ru(2)	0.25637(4)	0.14437(4)	0.22582(5)	*
Ru(3)	0.27793(4)	0.34757(4)	0.32441(5)	*
C(1)	−0.0407 (6)	0.2165 (6)	0.0898 (7)	3.5(2)
C(2)	−0.0423 (6)	0.3591 (6)	0.2764 (7)	3.0(1)
C(3)	0.2564 (6)	0.0052 (6)	0.2610 (6)	3.5(1)
C(4)	0.1668 (6)	0.0977 (5)	0.0687 (7)	3.3(1)
C(5)	0.2414 (6)	0.4675 (6)	0.4215 (7)	3.6(2)
C(6)	0.4301 (6)	0.3952 (6)	0.3672 (7)	3.2(1)
C(7)	0.4216 (6)	0.1132 (5)	0.1965 (6)	3.0(1)
C(8)	0.4672 (6)	0.1799 (5)	0.1386 (6)	2.7(1)
C(9)	0.5816 (6)	0.1865 (6)	0.1027 (7)	3.4(2)
C(10)	0.6505 (7)	0.2839 (7)	0.1749 (8)	4.8(2)
C(11)	0.5633 (8)	0.1919 (7)	−0.0355 (8)	4.9(2)
C(12)	0.6484 (7)	0.0887 (7)	0.1310 (8)	5.3(2)
C(13)	0.3007 (5)	0.2717 (5)	0.1437 (6)	2.4(1)
C(14)	0.2331 (5)	0.3627 (5)	0.1160 (6)	2.4(1)
C(15)	0.2678 (6)	0.4466 (6)	0.0425 (7)	3.4(1)
C(16)	0.2673 (8)	0.3904 (8)	−0.0894 (9)	5.5(2)
C(17)	0.3876 (8)	0.4992 (7)	0.1026 (9)	4.7(2)
C(18)	0.1814 (8)	0.5345 (7)	0.0328 (9)	5.3(2)
C(19)	0.1372 (6)	0.3695 (5)	0.1683 (6)	2.7(1)
C(20)	−0.0060 (6)	0.1090 (6)	0.2972 (7)	3.3(1)
C(21)	0.0648 (6)	0.1718 (5)	0.3992 (6)	2.9(1)
C(22)	0.0199 (6)	0.2135 (6)	0.5160 (7)	3.3(1)
C(23)	0.0627 (8)	0.1415 (7)	0.6133 (9)	5.3(2)
C(24)	0.0629 (7)	0.3258 (6)	0.5682 (7)	4.3(2)
C(25)	−0.1108 (8)	0.2094 (7)	0.4903 (8)	5.2(2)
C(26)	0.1774 (6)	0.1971 (5)	0.3813 (6)	2.7(1)
C(27)	0.2922 (5)	0.2247 (5)	0.4257 (6)	2.6(1)
C(28)	0.3814 (7)	0.1971 (6)	0.5348 (7)	3.7(2)
C(29)	0.3593 (9)	0.0851 (7)	0.5580 (9)	5.9(2)
C(30)	0.3752 (8)	0.2758 (7)	0.6491 (9)	5.6(2)
C(31)	0.5027 (8)	0.2028 (8)	0.5134 (9)	5.9(2)
O(1)	−0.0999 (6)	0.1940 (5)	−0.0164 (6)	6.1(2)
O(2)	−0.0986 (5)	0.4300 (4)	0.2967 (5)	4.7(1)
O(3)	0.2611 (6)	−0.0927 (5)	0.2735 (6)	5.9(1)
O(4)	0.1189 (5)	0.0655 (5)	−0.0320 (6)	5.7(1)
O(5)	0.2185 (6)	0.5427 (5)	0.4806 (6)	6.1(1)
O(6)	0.5234 (5)	0.4307 (5)	0.3874 (5)	5.3(1)
O(7)	0.3982 (4)	0.2643 (3)	0.1019 (4)	2.9(1)

*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	359(4)	339(4)	478(5)	39(3)	76(3)	85(3)
Ru(2)	415(4)	284(4)	439(5)	63(3)	88(3)	42(3)
Ru(3)	377(4)	433(5)	433(5)	49(3)	54(3)	20(3)

The tabulated β values are the $\beta_{ij} \times 10^4$ coefficients of the expression $\exp(-\sum_1^3 \sum_1^3 \beta_{ij} h_i h_j)$.

At this stage anisotropic thermal parameters were introduced for the ruthenium atoms and 3834 reflexions with $I > 2\sigma(I)$ were refined to $R = 0.046$; several residual peaks were located in the subsequent Fourier-difference map and 40 were attributed to the expected hydrogen atoms. A weighting factor $w = 4F_o^2/\sigma(F_o^2)^2$ was introduced and the anisotropic–isotropic refinement was made over 3687 reflexions with $I > 3\sigma(I)$ to $R = 0.037$, with only the positional parameters variable for the hydrogen atoms; the thermal parameters for the hydrogen atoms were assigned nearly one unit greater than those of the corresponding carbon atoms. The effects of anomalous dispersion of ruthenium were included in

TABLE II. Fractional Coordinates for Hydrogen Atoms.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(1)	0.48(1)	0.04(1)	0.24(1)	H(21)	0.02(1)	0.05(1)	0.25(1)
H(2)	0.73(1)	0.28(1)	0.16(1)	H(22)	−0.10(1)	0.11(1)	0.30(1)
H(3)	0.66(1)	0.28(1)	0.25(1)	H(23)	0.02(1)	0.16(1)	0.69(1)
H(4)	0.62(1)	0.35(1)	0.15(1)	H(24)	0.03(1)	0.08(1)	0.58(1)
H(5)	0.64(1)	0.21(1)	−0.05(1)	H(25)	0.13(1)	0.15(1)	0.64(1)
H(6)	0.55(1)	0.25(1)	−0.06(1)	H(26)	0.04(1)	0.38(1)	0.52(1)
H(7)	0.52(1)	0.15(1)	−0.09(1)	H(27)	0.04(1)	0.34(1)	0.65(1)
H(8)	0.73(1)	0.10(1)	0.11(1)	H(28)	0.14(1)	0.33(1)	0.58(1)
H(9)	0.77(1)	0.09(1)	0.20(1)	H(29)	−0.14(1)	0.24(1)	0.45(1)
H(10)	0.62(1)	0.04(1)	0.08(1)	H(30)	−0.14(1)	0.14(1)	0.48(1)
H(11)	0.20(1)	0.38(1)	−0.15(1)	H(31)	−0.15(1)	0.24(1)	0.58(1)
H(12)	0.29(1)	0.45(1)	−0.14(1)	H(32)	0.28(1)	0.07(1)	0.57(1)
H(13)	0.32(1)	0.34(1)	−0.09(1)	H(33)	0.40(1)	0.08(1)	0.65(1)
H(14)	0.38(1)	0.53(1)	0.17(1)	H(34)	0.36(1)	0.03(1)	0.48(1)
H(15)	0.42(1)	0.54(1)	0.03(1)	H(35)	0.32(1)	0.26(1)	0.67(1)
H(16)	0.44(1)	0.45(1)	0.10(1)	H(36)	0.40(1)	0.33(1)	0.64(1)
H(17)	0.20(1)	0.56(1)	0.10(1)	H(37)	0.45(1)	0.26(1)	0.72(1)
H(18)	0.14(1)	0.51(1)	0.00(1)	H(38)	0.57(1)	0.17(1)	0.59(1)
H(19)	0.20(1)	0.59(1)	−0.03(1)	H(39)	0.52(1)	0.26(1)	0.52(1)
H(20)	0.09(1)	0.43(1)	0.15(1)	H(40)	0.52(1)	0.16(1)	0.46(1)

TABLE III. Interatomic Distances (Å) for $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$.

		Ru–Ru Distances			
Ru(1)–Ru(2)	2.820(1)	Ru(1)–Ru(3)	2.828(1)	Ru(2)–Ru(3)	2.686(1)
		Ru–C Distances			
Ru(1)–C(1)	1.789(1)	Ru(2)–C(3)	1.888(7)	Ru(3)–C(5)	1.876(8)
Ru(1)–C(2)	1.857(7)	Ru(2)–C(4)	1.871(7)	Ru(3)–C(6)	1.854(7)
Ru(1)–C(19)	2.080(7)	Ru(2)–C(7)	2.102(7)	Ru(3)–C(13)	2.200(7)
Ru(1)–C(20)	2.253(7)	Ru(2)–C(13)	2.105(6)	Ru(3)–C(14)	2.320(7)
Ru(1)–C(21)	2.228(7)	Ru(2)–C(26)	2.188(7)	Ru(3)–C(19)	2.203(7)
Ru(1)–C(26)	2.163(7)	Ru(2)–C(27)	2.287(6)	Ru(3)–C(26)	2.497(7)
				Ru(3)–C(27)	2.058(6)
		C–C Distances			
C(7)–C(8)	1.324(10)	C(14)–C(19)	1.394(9)	C(22)–C(23)	1.536(12)
C(8)–C(9)	1.511(10)	C(15)–C(16)	1.555(13)	C(22)–C(24)	1.525(11)
C(9)–C(10)	1.526(11)	C(15)–C(17)	1.551(12)	C(22)–C(25)	1.525(12)
C(9)–C(11)	1.531(12)	C(15)–C(18)	1.537(12)	C(26)–C(27)	1.380(9)
C(9)–C(12)	1.531(11)	C(20)–C(21)	1.414(10)	C(27)–C(28)	1.526(10)
C(13)–C(14)	1.458(9)	C(21)–C(22)	1.552(10)	C(28)–C(29)	1.531(13)
C(14)–C(15)	1.551(10)	C(21)–C(26)	1.444(10)	C(28)–C(30)	1.537(12)
				C(28)–C(31)	1.523(13)
		C–O Distances			
C(1)–O(1)	1.243(11)	C(4)–O(4)	1.170(10)	C(8)–O(7)	1.422(8)
C(2)–O(2)	1.164(9)	C(5)–O(5)	1.166(10)	C(13)–O(7)	1.346(8)
C(3)–O(3)	1.160(10)	C(6)–O(6)	1.166(10)		

structure factor calculations using Cromer and Liberman's [12] values for Δf′ and Δf″. No correction for secondary extinction was made and no absorption correction was performed owing to the regular shape of the small crystal used.

Description of the Structure and Discussion

Atomic positional and thermal parameters for the non-hydrogen atoms of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ are given in Table I and hydrogen positional parameters are listed in Table II; interatomic distances

TABLE IV. Bond Angles (°) for $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$.

Ru–Ru–Ru Angles

Ru(2)–Ru(1)–Ru(3)	56.8(1)	Ru(1)–Ru(3)–Ru(2)	61.4(1)
Ru(1)–Ru(2)–Ru(3)	61.8(1)		

Ru–Ru–C Angles

Ru(2)–Ru(1)–C(1)	105.8(2)	Ru(3)–Ru(2)–C(4)	122.5(2)
Ru(2)–Ru(1)–C(2)	161.0(2)	Ru(3)–Ru(2)–C(7)	102.4(2)
Ru(2)–Ru(1)–C(19)	83.9(2)	Ru(3)–Ru(2)–C(13)	53.0(2)
Ru(2)–Ru(1)–C(20)	84.6(2)	Ru(3)–Ru(2)–C(26)	60.6(2)
Ru(2)–Ru(1)–C(21)	80.7(2)	Ru(3)–Ru(2)–C(27)	48.1(2)
Ru(2)–Ru(1)–C(26)	50.0(2)	Ru(1)–Ru(3)–C(5)	98.9(2)
Ru(3)–Ru(1)–C(1)	137.4(2)	Ru(1)–Ru(3)–C(6)	172.4(2)
Ru(3)–Ru(1)–C(2)	104.6(2)	Ru(1)–Ru(3)–C(13)	81.9(2)
Ru(3)–Ru(1)–C(19)	50.6(2)	Ru(1)–Ru(3)–C(14)	74.9(2)
Ru(3)–Ru(1)–C(20)	123.9(2)	Ru(1)–Ru(3)–C(19)	46.8(2)
Ru(3)–Ru(1)–C(21)	93.2(2)	Ru(1)–Ru(3)–C(26)	47.4(2)
Ru(3)–Ru(1)–C(26)	58.2(2)	Ru(1)–Ru(3)–C(27)	80.8(2)
Ru(1)–Ru(2)–C(3)	116.6(2)	Ru(2)–Ru(3)–C(5)	154.9(2)
Ru(1)–Ru(2)–C(4)	79.2(2)	Ru(2)–Ru(3)–C(6)	111.7(2)
Ru(1)–Ru(2)–C(7)	159.0(2)	Ru(2)–Ru(3)–C(13)	49.8(2)
Ru(1)–Ru(2)–C(13)	83.8(2)	Ru(2)–Ru(3)–C(14)	79.4(2)
Ru(1)–Ru(2)–C(26)	49.2(2)	Ru(2)–Ru(3)–C(19)	85.0(2)
Ru(1)–Ru(2)–C(27)	77.4(2)	Ru(2)–Ru(3)–C(26)	49.8(2)
Ru(3)–Ru(2)–C(3)	144.8(2)	Ru(2)–Ru(3)–C(27)	55.8(2)

C–Ru–C Angles

C(1)–Ru(1)–C(2)	90.7(3)	C(7)–Ru(2)–C(27)	109.2(2)
C(1)–Ru(1)–C(19)	92.4(3)	C(13)–Ru(2)–C(26)	111.3(3)
C(1)–Ru(1)–C(20)	87.9(3)	C(13)–Ru(2)–C(27)	98.3(2)
C(1)–Ru(1)–C(21)	124.3(3)	C(26)–Ru(2)–C(27)	35.8(2)
C(1)–Ru(1)–C(26)	143.7(3)	C(5)–Ru(3)–C(6)	88.6(3)
C(2)–Ru(1)–C(19)	86.1(3)	C(5)–Ru(3)–C(13)	148.6(3)
C(2)–Ru(1)–C(20)	105.8(3)	C(5)–Ru(3)–C(14)	112.1(3)
C(2)–Ru(1)–C(21)	98.0(3)	C(5)–Ru(3)–C(19)	92.2(3)
C(2)–Ru(1)–C(26)	119.3(3)	C(5)–Ru(3)–C(26)	105.8(3)
C(19)–Ru(1)–C(20)	168.1(3)	C(5)–Ru(3)–C(27)	108.5(3)
C(19)–Ru(1)–C(21)	142.9(3)	C(6)–Ru(3)–C(13)	91.0(3)
C(19)–Ru(1)–C(26)	108.4(3)	C(6)–Ru(3)–C(14)	101.1(3)
C(20)–Ru(1)–C(21)	36.8(3)	C(6)–Ru(3)–C(19)	132.0(3)
C(20)–Ru(1)–C(26)	65.8(3)	C(6)–Ru(3)–C(26)	131.8(3)
C(21)–Ru(1)–C(26)	38.4(3)	C(6)–Ru(3)–C(27)	98.2(3)
C(3)–Ru(2)–C(4)	89.1(3)	C(13)–Ru(3)–C(14)	37.5(2)
C(3)–Ru(2)–C(7)	84.4(3)	C(13)–Ru(3)–C(19)	65.4(2)
C(3)–Ru(2)–C(13)	53.0(2)	C(13)–Ru(3)–C(26)	97.8(2)
C(3)–Ru(2)–C(26)	91.0(3)	C(13)–Ru(3)–C(27)	102.6(2)
C(3)–Ru(2)–C(27)	96.7(3)	C(14)–Ru(3)–C(19)	35.8(2)
C(4)–Ru(2)–C(7)	100.8(3)	C(14)–Ru(3)–C(26)	114.5(2)
C(4)–Ru(2)–C(13)	84.2(3)	C(14)–Ru(3)–C(27)	135.1(2)
C(4)–Ru(2)–C(26)	121.2(3)	C(19)–Ru(3)–C(26)	94.0(2)
C(4)–Ru(2)–C(27)	156.0(3)	C(19)–Ru(3)–C(27)	126.4(2)
C(7)–Ru(2)–C(13)	75.4(3)	C(26)–Ru(3)–C(27)	33.5(2)
C(7)–Ru(2)–C(26)	137.7(3)		

Ru–C–C Angles

Ru(2)–C(7)–C(8)	116.7(5)	Ru(1)–C(26)–C(21)	73.3(4)
Ru(2)–C(13)–C(14)	127.8(5)	Ru(1)–C(26)–C(27)	129.3(5)
Ru(3)–C(13)–C(14)	75.7(4)	Ru(2)–C(26)–C(21)	129.5(5)
Ru(3)–C(14)–C(13)	66.8(4)	Ru(2)–C(26)–C(27)	76.0(4)

(continued on opposite page)

TABLE IV. *(continued)*

Ru(3)–C(14)–C(15)	131.9(5)	Ru(3)–C(26)–C(21)	137.8(5)
Ru(3)–C(14)–C(19)	67.5(4)	Ru(3)–C(26)–C(27)	55.5(3)
Ru(3)–C(19)–C(14)	76.7(4)	Ru(2)–C(27)–C(26)	68.2(4)
Ru(1)–C(20)–C(21)	70.6(4)	Ru(2)–C(27)–C(28)	127.8(5)
Ru(1)–C(21)–C(20)	72.6(4)	Ru(3)–C(27)–C(26)	91.0(4)
Ru(1)–C(21)–C(22)	125.3(3)	Ru(3)–C(27)–C(28)	133.6(5)
Ru(1)–C(21)–C(26)	68.4(4)		
	Ru–C–O Angles		
Ru(1)–C(1)–O(1)	174.1(7)	Ru(2)–C(13)–O(7)	116.3(4)
Ru(1)–C(2)–O(2)	174.2(6)	Ru(3)–C(5)–O(5)	179.2(0)
Ru(2)–C(3)–O(3)	173.7(7)	Ru(3)–C(6)–O(6)	174.6(7)
Ru(2)–C(4)–O(4)	174.5(7)	Ru(3)–C(13)–O(7)	127.8(4)
	C–C–C Angles		
C(7)–C(8)–C(9)	133.0(6)	C(20)–C(21)–C(26)	114.2(6)
C(8)–C(9)–C(10)	109.9(6)	C(22)–C(21)–C(26)	124.2(6)
C(8)–C(9)–C(11)	110.0(6)	C(21)–C(22)–C(23)	107.6(6)
C(8)–C(9)–C(12)	109.5(6)	C(21)–C(22)–C(24)	112.2(6)
C(10)–C(9)–C(11)	109.4(7)	C(21)–C(22)–C(25)	111.6(6)
C(10)–C(9)–C(12)	109.4(7)	C(23)–C(22)–C(24)	109.2(6)
C(11)–C(9)–C(12)	108.6(7)	C(23)–C(22)–C(25)	107.5(7)
C(13)–C(14)–C(15)	123.7(6)	C(24)–C(22)–C(25)	108.5(6)
C(13)–C(14)–C(19)	112.9(6)	C(21)–C(26)–C(27)	151.8(7)
C(15)–C(14)–C(19)	123.3(6)	C(26)–C(27)–C(28)	133.0(6)
C(14)–C(15)–C(16)	107.0(6)	C(27)–C(28)–C(29)	110.7(7)
C(14)–C(15)–C(17)	112.6(6)	C(27)–C(28)–C(30)	108.4(6)
C(14)–C(15)–C(18)	111.2(6)	C(27)–C(28)–C(31)	112.2(7)
C(16)–C(15)–C(17)	110.1(7)	C(29)–C(28)–C(30)	110.2(7)
C(16)–C(15)–C(18)	108.8(7)	C(29)–C(28)–C(31)	107.0(7)
C(17)–C(15)–C(18)	107.2(7)	C(30)–C(28)–C(31)	108.3(7)
C(20)–C(21)–C(22)	121.5(6)		
	C–C–O Angles		
C(7)–C(8)–O(7)	116.2(6)	C(14)–C(13)–O(7)	115.7(5)
C(9)–C(8)–O(7)	110.8(5)		
	C–O–C Angles		
C(8)–O(7)–C(13)	114.6(5)		

(Å) and bond angles (°) are tabulated in Tables III and IV, respectively. Two molecule views, each other nearly normal are shown in Fig. 1 and Fig. 2, including the atom labelling scheme.

The molecule consists of an isosceles three-ruthenium cluster with two terminal carbonyl groups bonded to each metal atom. Two organic ligands face-bridge the cluster on the opposite sides of the triangle. One of them derives from two acetylenic units joined via a –C–O– bridge, as clearly shown in Fig. 2 on the upper part of the cluster. The atoms of this ligand, together with Ru(1) and Ru(2) form two penta-atomic rings, joined along a side (Ru(2)–C(13)) and not strictly lying on a plane; the distances of the atoms from the calculated best plane range between 0.001 and 0.020 Å with the exception of the three atoms C(7), O(7) and C(19) (0.09, –0.10, 0.17 Å, respectively).

The second ligand derives from two head-to-tail joined acetylenic units with the shift of an hydrogen atom on C(20); the C(20), C(21), C(22), C(26), H(21), H(22) atoms lie on a plane inclined of 61° with respect to the C(26), C(27), C(28) plane, and of 12° with the C(26), C(27), Ru(2) plane. This chain is bonded to Ru(1) by means of C(20), C(21) and C(26), to Ru(2) by means of C(26) and C(27) and to Ru(3) by means of C(27).

Ru_3 Cluster and Carbonyl Groups

Ru(2)–Ru(3) is the shortest bond in the isosceles cluster and one of the shortest ever found in Ru compounds, near to the value of 2.702(5) and 2.698(3) Å

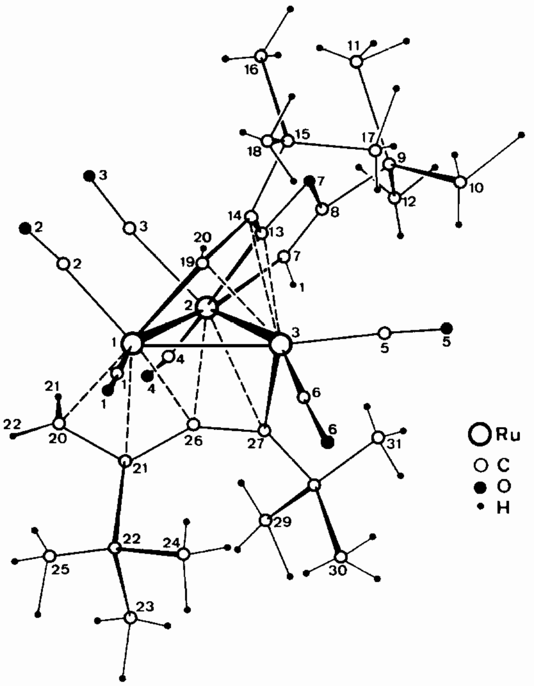

Figure 1. View of a molecule of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ with the atom labelling scheme.

of the non-bridged Ru–Ru bonds of monoclinic and triclinic $Ru_4(CO)_9[(CH_3)_3C_{10}H_5]$ [13, 14] respectively. Ru(2)–Ru(3) is doubly bridged by C(13) and C(27) and partially interacts with C(26), showing a very packed environment with respect to the other two Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds; actually these ones have mainly polyatomic bridges. No significant irregularity appears in carbonyl groups.

The $C_{12}H_{20}CO$ Ligand

In the penta-atomic C(13), C(14), C(19), Ru(1), Ru(2) ring there are two short (Ru(1)–C(19) and Ru(2)–C(13)) and three long (Ru(3)–C(13), Ru(3)–C(14) and Ru(3)–C(19)) Ru–C distances (Table III) as in the analogous $HRu_3(CO)_9(C_{13}H_9)$ [15], $HRu_3(CO)_9(C_{12}H_{15})$ [16], $HRu_3(CO)_9(C_6H_9)$ [17] and $Os_3(CO)_9(C_{15}H_{12}CO)$ [9] compounds. Although in our case the ring is only roughly planar with respect to the similar rings in the above mentioned compounds, the best calculated plane lies at 50° from the cluster as in the above cases. Therefore a π-coordination from the allylic C(13), C(14), C(19) group to Ru(3) and two σ-bonds (Ru(1)–C(19) and Ru(2)–C(13)) are postulated. In the allylic group a significant difference greater than σ is noteworthy between the C(13)–C(14) and C(14)–C(19) bond values, suggesting a prevalence of a single bond character for the C(13)–C(14) bond.

The penta-atomic C(7), C(8), O(7), C(13), Ru(2) adjacent ring (not a real plane chiefly because the C(13) atom is 0.14 Å outside) is bonded to the cluster only via two σ-bonds (Ru(2)–C(7) and Ru(2)–C(13)). The C(7)–C(8) distance (1.324(10) Å) is consistent with a double bond character; the C(13)–O(7) bond (1.346(8) Å) is significantly shorter than a single C–O bond, while the C(8)–O(7) distance (1.422(8) Å) is nearer to a single-bond order. On the basis of the above considerations and taking in account that the C(13) atom protrudes by 0.039 Å only from the best plane through the atoms Ru(2), C(13), C(14) and O(7), and that the arrangement around C(13) is much closer to a trigonal-planar configuration than to a tetrahedral one, C(13) can be correctly considered as a carbene carbon atom [18]. Since the three Ru–C bonds are only slightly longer than the $Ru–C_{CO}$ bonds a partial double-bond character can be postulated, as in $HRu_3(CO)_9(C_{13}H_9)$, $HRu_3(CO)_9(C_{12}H_{15})$, $HRu_3(CO)_9(C_6H_9)$ and $Os_3(CO)_9(C_{15}H_{12}CO)$ compounds.

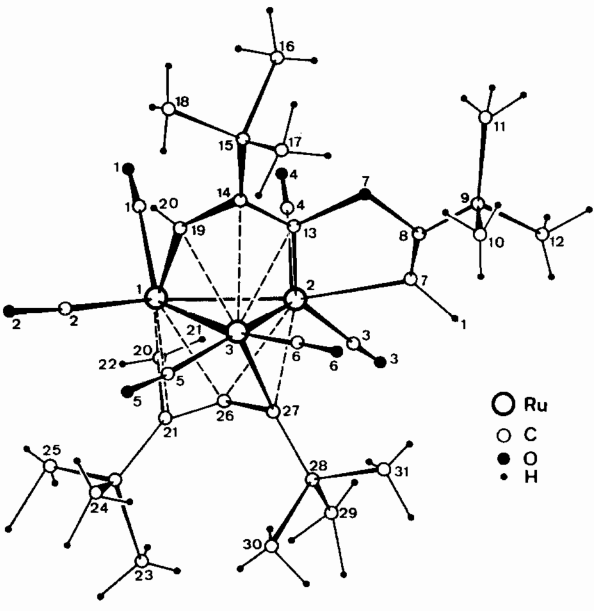

Figure 2. View of a molecule of $Ru_3(CO)_6(C_{12}H_{20}CO)(C_{12}H_{20})$ showing the two penta-atomic rings involving the $C_{12}H_{20}CO$ ligand.

The $C_{12}H_{20}$ Ligand

As in $Fe_2(CO)_6(C_9H_{14}CO)$ and $Fe_2(CO)_6(C_7H_{10}CO)$ [20], an open chain (C(20), C(21), C(26), C(27)) of the $C_{12}H_{20}$ ligand is coordinated to the cluster. The chain C–C distances show no highly significant difference and no double bond is hence localized on the basis of the distance values. The C(20), C(21), C(22), C(26), H(21) and H(22) atoms lie on a plane at 49° from the cluster plane; an sp^2 hybridization of C(20) and C(21) satisfactorily agrees with the planarity and the angles involved. The three distances Ru(1)–C(20), Ru(1)–C(21), Ru(1)–C(26) are in the long–long–short sequence for the distortion due to the multi-coordination of the C(26) atom, as found in the Cotton mentioned compounds [20], where an η^3-allylic-M description seems suitable. The C(26)–C(27) bond has the intermediate value between a double and a single bond of the metal-coordinated double bonds and is unsymmetrical with respect to Ru(2)–Ru(3). The C(26), C(27), C(28) and Ru(3) atoms form a roughly planar group at 70° from the C(20), C(21), C(26) plane, near to the expected orthogonality. The linkage between the C(26)–C(27) bond and the cluster is realized through a σ-bond (Ru(3)–C(27)) and a π-coordination towards Ru(2). The arrangement around the C(20), C(21) and C(27) atoms agrees with an sp^2 hybridization, while for C(26) a distorted sp hybridization is more suitable.

Eventually it is interesting to note that as consequence of the head-to-tail joining of the two alkynic units C(26) has no hydrogen bonded and a CH_2 group is formed (C(20)), this agrees with the hydrogen shift hypothesis postulated on the basis of n.m.r. data [2], and hence with the supposed reaction mechanism that gives rise to the title compound from $HRu_3(CO)_9[(C_2C(CH_3)_3]$ and 3,3-dimethyl-1-butyne [2].

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Supplementary Material Available

Copies of the observed and calculated structure factors are available from G. G. upon request.

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